

## Fusible and heat-curable solidly materials, useful as the basis of coating powders for plastics, glass, ceramics and especially metals

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### Abstract of DE19817785

Fusible and heat-curable solidly materials based on condensates with a viscosity minimum of 10 mPa.s to 150 Pa.s in the range 50-200 deg C, derived from hydrolysable silanes (and possibly hydrolysable metal compounds) containing groups which enable further condensation and non-hydrolysable organic groups. Fusible and heat-curable solidly materials comprise condensates (K) derived from hydrolysable silane (s) and optionally hydrolysable metal compound (s), with central atoms (M) linked to groups (A) which facilitate further condensation of (K) and with non-hydrolysable organic groups (R) on at leastes 70% of the atoms (M), these groups (R) being partly replaceable by complex-forming species co-ordinated with (M). The viscosity of (K) passes through a minimum value of 10 mPa.s to 150 Pa.s in the range 50-200 deg C. Independently claims are included for (a) a process for coating substrates with coating powder based on these materials; (b) a process for the production of these materials by controlled hydrolytic condensation of hydrolysable silicon compounds and / or corresponding silanols with some non-hydrolysable groups (R), optionally with hydrolysable metal compounds, to give condensates with the above viscosity characteristics, followed by removal of any volatiles.

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### Description of DE19817785

The present invention concerns a steady, aufschmelzbare and thermally härtbare inorganic-organic mass, production as well as their use.

The use of powder varnish has asserted itself in wide measure, because these can release substantially small quantities in brief components in contrast to applied an as a solution to coating systems and be started with it substantially more environmental-acceptably. The powder varnish exists as a rule of thermo-sculptural (organic) full polymer particles which can be raised on a substrate surface and dissolve afterwards by warming up. A thick layer originates from it. Nevertheless, a disadvantage of such powder varnish is that they are not suitable because of the qualities of the polymers constructing them for many uses or only partly. One of these disadvantageous qualities is a gradual Erweichungsverhalten which allows a flowable phase only at relatively high temperatures, and, partly by the high viscosity also still being at these high temperatures, the necessity to the application of thick layers (minimally from 80 to 100 mu m). In addition, thermo-sculptural materials are marked by her relatively bad mechanical qualities. This applies in particular to the wear and Kratzfestigkeit.

Indeed, the reactive systems, especially those which are characterised by the construction of an inorganic network (e.g., about Sol gel colleges of technology made inorganic-organic Kompositwerkstoffe) own excellent mechanical qualities and show high wear firmness, nevertheless, are not thermo-sculptural, because the inorganic network is spontaneously built up and already leads with ambient temperature to so high condensation degrees that no Thermoplastizität can appear.

Now it was found astonishing-wise that it is possible to stop the education of (Hetero) polykondensaten on the base from hydrolysierbaren Silanen and if necessary other hydrolysierbaren (metal) verbindungen at such a low interlinking degree (condensation degree) that the suitable condensates result as aufschmelzbare solids which can be hardened to a niedrigviskosen cover aufgeschmolzen and as a result thermally (and if necessary, in addition, also photo-chemically) by other condensation and if necessary by reaction of available organic groups. Besides, stopping the education of the (Hetero) polykondensate on a low interlinking degree can be managed by a row of the measures which are explained below closer.

The object of the present invention is a steady, aufschmelzbare and thermally härtbare mass which encloses derived condensates K of at least to one hydrolysierbaren Silan and if necessary to one or several hydrolysierbaren metal connections and (1) to itself in central atoms M of the condensates K find groups A which allow a wide condensation of the condensates, (2) at least 70% of the central atoms M one or several not hydrolysierbare organic groups R engaged in it show from which a part can be substituted by with the central atoms M of co-ordinated complicated-pedagogic species, and (3) the condensates K in the temperature area by from 50 to 200 C DEG a viscosity minimum in the area of 10 mPa.s to 150 Pa.s go through.

The above mass is suited, for example, as a powder varnish to the coating of substrates, e.g., to the production of a wear-steady and anti-corrosive coating on metals, for example, as a (clear) covering lacquer (e.g., about a polyurethane-base varnish) in the car industry.

In the following the present invention is explained with reference to preferential execution forms to the same closer.

With to the condensates K basic monomeren to hydrolysierbaren connections it gets mainly around or several hydrolysierbare Silane, in particular Silane of the general formula R<sub>n</sub>SiX<sub>4-n</sub>, in what R an organic group defined closer explains which groups X, immediately or can have passed away and mainly are identical, hydrolysierbare rests can show and accept n the value 1, 2 or 3, mainly 1 or 2 and especially preferentially 1. The rests X are selected mainly from halogen atoms (in particular chlorine and bromine), Alkoxygruppen, Alkylcarbonylgruppen and Acyloxygruppen and Alkoxygruppen, in particular C1-4-Alkoxygruppen are especially preferred like Methoxy and Ethoxy.

Under used hydrolysierbaren Silanen a small part (mainly less than 5 Mol-% can also be on the basis of all used monomeren to hydrolysierbaren connections) in Silanen of the above formula in which n immediately 0 are.

Beside at least one hydrolysierbaren Silan to applicable hydrolysierbaren metal connections are mainly those which are derived from metals of the main groups IIIa and IVa as well as the Nebengruppen IVb, Vb and VIb of the periodic system and connections are especially preferred by aluminium, titanium and zirconium. With the hydrolysierbaren connections of the last-called elements it concerns taking into account theirs with the Hydrolyse and condensation substantially higher reactivity than that of the silicon connections mainly around complex connections and on applicable Komplexbildner will be entered further below even closer. Should suitable more active connections, e.g., the alc. oxide be used by Al, Ti and/or Zr, must not be provided by suitable measures for the fact, that the high reactivity of these connections to problems with the setting of the desired condensation degree or. of the desired viscosity course leads, e.g., by work at low

temperature (e.g., 0 C DEG or under it) and/or application in small quantities and/or under strong thinner.

Mainly are in the condensates used in the erfundungsgemäßen mass K at least 75, in particular at least 85 and especially prefers at least 95% (including 100%) of the central atoms M as silicon atoms and the rest on 100% of the remaining used hydrolysierbaren metal connections, in particular connections of Al, Ti and Zr, comes.

Preferential condensates K contain at least 5, mainly at least 10 and in particular at least 20 central atoms M. The number of the central atoms M can amount, e.g., up to 300, mainly up to 200 and in particular up to 150. The central atoms M are connected mainly about oxygen bridges. Further it is preferred that at least 70 and mainly at least 80% of the central atoms M about at least one did not substitute (with complicated-pedagogic species) for organic group R dispose and the whole rest of the central atoms M is co-ordinated mainly with complicated-pedagogic species.

In the end, it is also preferred, if the numerical ratio x in the condensates K to available central atoms M to the sum in these central atoms to located ones, a wide condensation (inorganic interlinking) to allowing groups A in the area by 1: From 2 to 20: 1, in particular 1: From 1 to 10: 1, especially prefers 2: From 1 to 5: 1, lies. With these groups A in the central atoms M it concerns mainly around Hydroxy-, Alkoxy, Aryloxy-, Acyloxy-(e.g., Acetoxy), Enoxy-or Oximgruppen. Mainly there are at least 80% of one wide condensation to allowing connection places in the central atoms M of groups A (e.g., hydroxyl groups), while the remaining connection places are blocked by complicated-pedagogic species. Suitable Komplexbildner are, for example, Chelat-Bildner like beta-Diketone (e.g., Acetylacetone), beta-Ketoester (e.g., Acetylacetate), organic acids (e.g. Acetic acid, Propionic acid, acrylic acid, Methacrylic acid), alpha-Hydroxycarboxylic acids (e.g., alpha-Hydroxypropionic acid), but also inorganic complicated-pedagogic species as for example Fluorid-, Thiocyanat-, Cyanat-and Cyanidionen as well as ammonia and quartäre ammonium salts as for example Tetraalkylammoniumsalze (chloride, bromide, Hydroxide etc.), for example, Tetramethyl and Tetrahexylammoniumsalze.

Beside the abovementioned central atoms M which are derived mainly from Si, Al, Ti and Zr the condensates can show K final groups with alkali and/or alkaline earth metal atoms.

To favour the education of the condensates used in the erfundungsgemäßen mass K with the desired viscosity behaviour, relatively low condensation degree and a relatively low relation of central atoms to connection places capable for the wide condensation, different measures or combinations the same can be used. For example, it is possible, as already on top mentioned, to carry out the polycondensation at relatively low temperatures and/or under strong thinner (monomeren) to hydrolysierbaren source connections and/or with strongly shortened condensation times. Nevertheless, Erfundungsgemäß are preferred other measures, in particular (With) verwendung by hydrolysierbaren source connections, condensation by sterically demanding (re) organic groups R with ambient temperature Be or, it is prevented, but can run off with to the Aufschmelzen of the erfundungsgemäßen mass of necessary raised temperatures (and about that) just like that. Next erfundungsgemäß the preferential measure which can be used alternatively or in addition to the already called measures is the annexation of one or several substances in the erfundungsgemäße mass which releases a catalyst for the condensation of the still available connection places capable of condensation (in particular an acid or base) with to the Aufschmelzen of the mass of necessary raised temperatures (or even even higher temperatures).

In the end, consists in it an other preferential erfundungsgemäße measure which can be used likewise alternatively or in addition to the other measures, to use hydrolysierbare source connections with organic groups R which catalyzed with to the Aufschmelzen of the mass of necessary raised temperatures (or being higher temperatures) with her equals or other reactive organic groups R (if necessary) reaction can come which leads to an organic interlinking of the

available condensates. In this case it is possible, for example to annex to the erfundungsgemässen mass thermal Polymerisations-(polyaddition) or polycondensation catalyst which is activated only with to the Aufschmelzen of the erfundungsgemässen mass of necessary temperatures (or about that). Thus K (= wide condensation) can occur beside the inorganic interlinking of the condensates also an additional organic interlinking of these condensates. Of course it is also possible to carry out a such organic interlinking photo-chemically (mainly with added photo initiator and with UV radiotherapy) and in addition to a thermal Härtung (e.g., following that).

The measures demonstrated on top are explained in the following closer.

Unwieldy organic groups R, as for example are suited for the steric impediment or prevention of the condensation of hydrolysieren species with ambient temperature or a temperature which is necessary for the later necessary distance of brief components from the reaction mixture under education of a steady mass if necessary substituted C6-10-Arylgruppen and (cyclo) aliphatische groups which deliver a sterically obstruction which corresponds at least of those one Isopropylgruppe. For this purpose erfundungsgemäß preferential groups R are (if necessary substituted) Phenylgruppen. Accordingly a preferential group of hydrolysierbaren source connections for the production of the condensates is a K that hydrolysierbaren Phenylsilane and Diphenylsilane, e.g. Phenyltrimethoxsilan and Phenyltriethoxsilan and the suitable Diphenyl connections, but also the connections hydrolysieren completely or already partially as for example Diphenylsilandiol. In addition, or alternatively for the supply of sterically demanding groups R (in particular in the silicon atom) it is also possible to intend thermo-unstable organic groups R in the source connections, e.g., Ethylgruppen and vinyl groups which decompose at raised temperatures and thereby the way for a (direct) linking of the central atoms to which they were bound take time off. Therefore an other preferential group of source connections for the erfundungsgemäß used condensates passes K of Silanen with for example Ethyl or vinyl groups, e.g., Ethyltri (m) ethoxysilan and Vinyltri (m) ethoxysilan.

The organic interlinking mentioned on top of the erfundungsgemäß used condensates can be managed, for example, by the fact that one goes out from hydrolysierbaren source connections (mainly silicon connections) which dispose of organic rests R which enter (chains) reaktion at higher temperatures either from themselves or with the help of a catalyst activated at these higher temperatures. In this connection in particular epoxyhaltige groups R and groups R which show a reactive carbon carbon-multiple connection (in particular double connection) would be to be called. Concrete and preferential examples of such rests R are Glycidoxyalkyl-and (Meth) acryloxyalkyl leftovers which are bound mainly to a silicon atom and show mainly from 1 to 6 carbon atoms in the Alkyl rest, in particular Glycidoxypropyl-and Methacryloxypropylgruppen. Accordingly an other group of preferentially used hydrolysierbaren source connections exists of Glycidoxyalkyltri (m) ethoxysilan and Methacryloxyalkyltri (m) ethoxysilan. Of course it is also possible, source connections with different groups R which can react with each other to start, as for example groups R with carbon carbon-multiple connection and groups R with a SH group (which can add itself at raised temperatures and if necessary catalysis to the carbon carbon-multiple connection) or groups R with an Epoxid ring and groups R with an amino group. Quite in general groups R or combinations can be used by groups R which can come at raised temperatures if necessary catalyzed Polymerisations-(polyaddition) or polycondensation reaction. Besides, polyaddition reactions (including Polymerisationsreaktionen) are preferred, because they lead in contrast to condensation reactions to no by-products. In a such case it can be advisable if necessary to produce polycondensates with groups R reactive with each other apart and only when to combine solids with each other.

As already on top explains closer, an other measure consists to the setting of the desired viscosity course or to the inhibition of the other condensation of the used condensates K with ambient temperature or easily raised temperature in blocking places capable of condensation in the central atoms by complicated-pedagogic species and the suitable complexes are removed with to the Aufschmelzen of the erfundungsgemässen mass of necessary temperatures (or about

that) and free with it the way for an other condensation. For this purpose suitable Komplexbildner were already given on top. Such Komplexbildner are used mainly in combination with the metal connections which differ (in the central atom) from hydrolysierbaren Silanen, however, can be used also in form komplexierter Silane.

A possibility to promote the wide condensation of the erfundungsgemäss used condensates K at raised or high temperatures and to put in this manner the desired viscosity behaviour consists in annexing one or several substances to the erfundungsgemässen mass which split off catalytic active species at raised temperatures concerning the condensation or release. Examples of such catalytic active species are protons, hydroxyl ions, Fluoridionen and the like. For example, Tetraalkylammoniumsalze release more than 160 C DEG the tertiäre amine which is effective likewise catalytic at temperatures. As already mentioned, the same principle can be also applied to the organic interlinking, namely while one in the erfundungsgemässen mass, e.g. a thermally activateable radical starter, as for example a Peroxid or an Azo connection, annexes which initiates then the thermal Polymerisation more accordingly of organic groups R.

Beside above to the production of the erfundungsgemässen mass of essential or preferential components other components can be also added to this mass of course or be annexed to this to achieve, in addition, other desirable qualities. For example, it is possible to use those with rests fluoridated all or part R as a part of the too hydrolysierenden source connections to reach to covers with hydro- and oleophoben qualities. As suitable source connections would be to be called here, for example, Trialkoxysilane with 2-(mainly C2-12-) Perfluoralkylethyl rest. Another possibility for the introduction of fluorine atoms in the erfundungsgemässen mass exists, e.g., in the use of Perfluorcarbonsäuren (for example, as complicated-pedagogic species) or from fluoridated organic Copolymeren (see below).

If an organic interlinking of the condensates used in the erfundungsgemässen mass K is intended with the help of at raised temperatures (or with radiotherapy) to a polypolyaddition or condensation reaction to capable groups R, it can turn out useful to annex suitable purely organic monomers to the erfundungsgemässen mass also which are mainly steady with ambient temperature and can be incorporated in the polypolyaddition or condensation reaction of the suitable organic groups R, e.g., Caprolactam, Maleinsäure or Pyromellitsäuredianhydrid. The same also applies to the possible annexation of polymers in the erfundungsgemässen mass and in this connection, e.g., Silan-funktionalisierte polyester and other powder varnish materials would be to be called.

The erfundungsgemässen mass can also contain usual fillers. Especially the installation from nanopartikulären, if necessary to surfaces-modified oxide powders (particle size mainly up to 200 nm is preferred, in particular up to 100 nm), as for example such of Siliciumdioxid, aluminium oxide (in particular Böhmit) and zirconium oxide. These nanopartikulären oxide powders can be annexed either already during the production of the condensates and/or after their production to the erfundungsgemässen mass.

Of course the erfundungsgemässen mass can also contain other additions usual for powder varnish, as for example course additives, Glanzbildner, colorings, pigments and the like. Nevertheless, preferentially the erfundungsgemässen mass passes K to at least 50 Gew.-% and in particular to at least 80 Gew.-% of the above condensates. Fillers and/or the nanopartikulären oxide powders mentioned on top are used mainly in an amount from up to 25 Gew.-%, in particular up to 15 Gew.-%.

The production of the erfundungsgemässen mass can occur through the expert in this area familiar procedures, e.g., the Sol gel process. A distance of the brief auxiliary materials used in the course of the production procedure (e.g., organic solvents and waters) and the brief materials educated during the procedure (e.g., alcohols in case of the Hydrolyse of alc. oxide) joins this. This distance likewise occurs with the help of current procedures and devices, as for example rotation evaporator, thin layer evaporator, spray dryer and the like.

After distance of the brief components under preservation of a steady mass this can be processed if necessary on a suitable grain size or a suitable grain dimensions distribution, for example, by meals, seven and the like.

The application of the so preserved mass (powder varnish) for the coating of substrates, in particular such from metals, plastics, glass and ceramics, can likewise occur with the help of known procedures, mainly however, through electrostatic powder varnish.

The following examples serve the other illustration of the present invention. Within the scope of the invention the viscosity of the condensates K is measured according to the norms German Institute for Standardization 1342 T1 and T2 as well as German Institute for Standardization 53018 T1 under use of a Rotationsviskosimeters ("Rheolab MC 20" of the fa Physica Messtechnik GmbH and Co. KG, D-70567 Stuttgart) with cone record geometry according to German Institute for Standardization 53018 T1 (cone corner 2 DEG). Two measuring systems are applied:

Measuring system 1: Cone radius 1.25 cm; applicable for viscosity measuring areas of from 0.5 to 3200 Pa.s;

Measuring system 2: Cone radius 3.75 cm; applicable for viscosity measuring areas of from 0.02 to 120 Pa.s.

The measuring system 2 allows in the viscosity area below 1 Pa.s more exact measurements than the measuring system 1. In the overlapping area of both measuring systems identical viscosity values will receive with the same condensates and at the same temperature. In all cases occurs the viscosity measurement with a mole rate of 1.05 rad/see and a heating rate of 2 K / Min in the temperature area of from 50 to 200 C DEG.

#### Example 1

14.82 gs (0.1 Mol) Vinyltrimethoxysilan were moved with 48.87 gs (0.2 Mol) Diphenyldimethoxysilan. Under strong touching were given to the mixture drop by drop 37.8 gs 0.1 n HCl. Besides, a light warming appeared. After finished addition became with ambient temperature 1 h weitergerührt. With increasing response time a white, steady mass formed from the at first available suspension. The product became with 40 C DEG and a final pressure of approx. 5-6 mbar 1 h abrotiert. On this occasion, one receives a rieselfähiges powder with a viscosity minimum from 0.02 to 0.03 Pa.s at a glaze temperature of 172 C DEG.

The powder was pretreated after a meal process (Red Devil, fa Erichsen) electrostatically (hand spray gun, fa Wagner-ESB) on aluminium tins (Al 99.5 mill finish, with alkaline Tensid (Almeco TM , fa handle)) applied.

The coated Al tins were hardened 30 min with 170 C DEG in the Umlufttrockenschrank. The resultant smooth, clear coating of 35 around thickness showed quasi-thermosetting behaviour what was proved by DSC investigations (DSC 200, fa Netsch).

#### Example 2

24.8 gs (0.1 Mol) Methacryloxypropyltrimethoxysilan (MPTS) were moved with 73.3 gs (0.3 Mol) Diphenyldimethoxysilan. Under strong touching a mixture of 1.2 gs (0.02 Mol) gamma-AIO (OH) and 73 gs 0.1 n HCl was let drip to the mixture. Besides, a clear warming appeared. The Dispergierung gamma-AIO (OH) in the watery medium occurred in the form that at first the watery HCl solution was presented, afterwards under strong touching gamma-AIO (OH) (Disperal TM Sol

P3, fa.

Condea) was slowly added and finally the suspension approx. 20 min with ambient temperature ultrasonic-treated became.

After finished addition watery gamma-AlO (OH) solution became with ambient temperature 15 min weitergerührt. With increasing response time a white, steady mass formed on the at first available suspension. The product became with 40 C DEG and a final pressure of approx. 5-6 mbar 1 h abrotiert. On this occasion, one receives a not rieselfähiges powder with a viscosity minimum from 0.02 to 0.04 Pa.s at a glaze temperature of 147 C DEG.

The powder became steady on aluminium tins (Al 99.5 mill finish, pretreated with alkaline Tensid (Almeco TM , fa handle)) applied and 30 min with 170 C DEG in the Umlufttrockenschrank hardened.

The resultant clear coating showed quasi-thermosetting behaviour what was proved by DSC investigations.

### Example 3

14,82 gs (0.1 Mol) Vinyltrimethoxysilan were moved with 61.09 gs (0.25 Mol) Diphenyldimethoxysilan. Under strong touching a mixture of 1.2 gs (0,0047 Mol) N Trimethoxysilylpropyl N, N, N trimethylammonium chloride and 45.5 gs 0.1 n HCl was let drip to the mixture. Besides, a light warming appeared. After finished addition became with ambient temperature 1 h weitergerührt. With increasing response time a white, steady mass formed from the at first available suspension. The product became with 40 C DEG and a final pressure of approx. 5-6 mbar 1 h abrotiert. On this occasion, one receives a rieselfähiges powder with a viscosity minimum from 0.3 to 1.8 Pa.s at a glaze temperature of 90 C DEG.

The powder became steady on aluminium tins (Al 99.5 mill finish, pretreated with alkaline Tensid (Almeco TM fa handle)) applied and 30 min with 170 C DEG in the Umlufttrockenschrank hardened what was proved by DSC investigations.

### Example 4

In 50 ml-round pistons became 0,015 Mol techn. Zirkoniumtetra-n-propylat-Lösung in n-Propanol presented (gravimetrisch certain content in Zr [OPr] 4: 77.3 Gew.-%). To the Zirkoniumtetra-n-propylat became under stirring 0,015 Mol Methacrylsäure slowly zugetropft and an easily exotherme reaction appeared. The reaction mixture was stirred lichtgeschützt 30 min in the close piston and afterwards was processed directly.

14,82 gs (0.1 Mol) Vinyltrimethoxysilan were moved with 48.87 gs (0.2 Mol) Diphenyldimethoxysilan. Under touching it was described to this mixture as on top made Zirkoniumtetra-n-propylat/Methacrylsäure-Mischung zugetropft.

Under strong touching were given to the resultant reaction mixture drop by drop 40 gs 0.1 n HCl. Besides, a light warming appeared. After finished addition became with ambient temperature 1 h lichtgeschützt weitergerührt. With increasing response time a white, steady mass formed from the at first available suspension. The product became with 40 C DEG and a final pressure of approx. 5-6 mbar 1 h abrotiert. On this occasion, one receives a rieselfähiges powder with a viscosity minimum from 0.03 to 0.1 Pa.s at a glaze temperature of 93 C DEG.

The powder was covered with 2 Gew.-% Benzoin (to the ready powder) dearly mixed and after a meal process steadily on aluminium tins (Al 99.5 mill finish, pretreated with alkaline Tensid (Almeco TM , fa handle)) applied and 30 min with 170 C DEG in the Umlufttrockenschrank hardened what was proved by DSC investigations.

#### Example 5

39,66 gs (0.2 Mol) Phenyltrimethoxysilan, 14.82 gs (0.1 Mol) Vinyltrimethoxysilan and 97.74 gs (0.4 Mol) Diphenyldimethoxysilan became in the given order eingewogen. Under strong touching were given to the mixture drop by drop 91.8 gs 0.1 n HCl. Besides, a light warming appeared. After finished addition became with ambient temperature 1 h weitergerührt. With increasing response time a white, steady mass forms from the at first available suspension. The product became with 40 C DEG and a final pressure of approx. 5-6 mbar 1 h abrotiert. On this occasion, one receives a rieselfähiges powder with a viscosity minimum from 0.1 to 0.3 Pa.s at a glaze temperature of 100 C DEG.

The powder became steady on aluminium tins (Al 99.5 mill finish, pretreated with alkaline Tensid (Almeco TM , fa handle)) applied and 30 min with 160 C DEG in the Umlufttrockenschrank hardened what was proved by DSC investigations.

#### Example 6

24,63 gs (0.1 Mol) [beta - (3,4-Epoxyhexyl) ethyl] trimethoxysilan (ETMS) were moved under strong stirring with ambient temperature with 24.44 gs (0.1 Mol) Diphenyldimethoxysilan (DPDMS) (mixture A). In parallel a mixture B was produced as follows: To 18 gs 0.1 n HCl were given under strong touching 0.36 gs (0,006 Mol) gamma-AlO (OH) in helpings. For the originating clear solution were added afterwards under strong touching 11.61 gs (0.1 Mol) Maleinsäure in helpings. After finished addition became with ambient temperature 10 min weitergerührt, until a clear mixture had originated.

Under strong touching and ice cooling mixture B was min given to mixture A drop by drop within 30. After finished addition became 4 h with ambient temperature weitergerührt. With increasing response time a white, steady mass formed from the at first available suspension. The product was dried with 40 C DEG and a final pressure from 10-20 mbar 0.5 h abrotiert, 5 h in the Umlufttrockenschrank under vacuum (7 mbar, 45 DEG C) and submitted to a meal process (Red Devil, fa Erichsen). On this occasion, one receives a rieselfähiges powder with a viscosity minimum from 4.3 to 8.6 Pa.s at a glaze temperature of 90 C DEG, a middle density of 1.29 gs / cm <3> and a grain dimensions distribution from 20-100 mu m. The powder shows thermosetting behaviour after the glaze process what was proved by DSC investigations. The coating powder is electrostatic with a conventional hand spray gun (fa. Wagner-ESB) on aluminium tins (Al 99.5 mill finish, fa pretreated with alkaline Tensid (Almeco TM handle)) applicable. The coated aluminium tins were treated 20 min with 130 C DEG in the Umlufttrockenschrank thermally. The resultant closed, clear cover from 10-20 mu m of thickness shows good liability (Gt 0/1, TT 0/1).

#### Example 7

24,63 gs (0.1 Mol) (beta - (3,4-Epoxyhexyl) ethyl) trimethoxysilan (ETMS) were moved under strong stirring with ambient temperature with 24.44 gs (0.1 Mol) Diphenyldimethoxysilan (DPDMS). For this solution were given in helpings 26.88 gs (0,025 Mol) well gemörseretes Poly (Bisphenol A-co-epichlorhydrin)-glycidyl endcapped (Mn approx. 1075). After approx. 15 min

originated a clear solution (mixture A). In parallel a mixture B was produced as follows: To 18 gs 0.1 n HCl were added under strong touching 11.61 gs (0.1 Mol) Maleinsäure in helpings. After finished addition became with ambient temperature 10 min weitergerührt, so that a clear mixture originated.

Under strong touching and ice cooling mixture B was min given to mixture A drop by drop within 30. After finished addition became 4 h with ambient temperature weitergerührt. With increasing response time a white, steady mass formed from the at first available suspension. The product was dried with 40 C DEG and a final pressure from 10-20 mbar 0.5 h abrotiert, 5 h in the Umlufttrockenschrank under vacuum (7 mbar, 45 DEG C) and submitted to a meal process (Red Devil, fa Erichsen). On this occasion, one receives a rieselfähiges powder with a viscosity minimum from 10 Pa.s at a glaze temperature of 93 C DEG, a middle density of 1.29 gs / cm <3> and a grain dimensions distribution from 20-100 mu m. The powder shows thermosetting behaviour after the glaze process what was proved by DSC investigations. The coating powder is electrostatic with a conventional hand spray gun (fa. Wagner-ESB) on aluminium tins (Al 99.5 mill finish, fa pretreated with alkaline Tensid (Almeco TM handle)) applicable. The coated aluminium tins were treated 20 min with 130 C DEG in the Umlufttrockenschrank thermally. The resultant closed, clear cover from 10-20 mu m of thickness shows good liability (Gt 0/1, TT 0/1).

#### Example 8

24.63 gs (0.1 Mol) [beta - (3.4-Epoxydicyclohexyl) ethyl] trimethoxysilan (ETMS) were moved under strong stirring with ambient temperature with 24.44 gs (0.1 Mol) Diphenyldimethoxysilan (DPDMS) (mixture A). In parallel a mixture B was produced as follows: To 18 gs 0.1 n HCl 11.61 gs (0.1 Mol) Maleinsäure were added in helpings. After finished addition became with ambient temperature 10 min weitergerührt, until a clear mixture had originated.

Under strong touching and ice cooling mixture B was min given to mixture A drop by drop within 30. After finished addition became 4 h with ambient temperature weitergerührt. With increasing response time a white, steady mass formed from the at first available suspension. The product was dried with 40 C DEG and a final pressure from 10-20 mbar 0.5 h abrotiert, 5 h in the Umlufttrockenschrank under vacuum (7 mbar, 45 DEG C) and submitted to a meal process (Red Devil, fa Erichsen). On this occasion, one receives a rieselfähiges powder with a viscosity minimum from 13.3 Pa.s at a glaze temperature of 102 C DEG, a middle density of 1.29 gs / cm <3> and a grain dimensions distribution from 20-100 mu m. The powder shows thermosetting behaviour after the glaze process what was proved by DSC investigations. The coating powder is electrostatic with a conventional hand spray gun (fa. Wagner-ESB) on aluminium tins (Al 99.5 mill finish, pretreated with alkaline Tensid (Almeco TM , fa handle)) applicable. The coated aluminium tins were treated 20 min with 130 C DEG in the Umlufttrockenschrank thermally. The resultant closed, clear cover from 10-20 mu m of thickness shows good liability (Gt 0/1, TT 0/1).

#### Example 9

24.63 gs (0.1 Mol) [beta - (3.4-Epoxydicyclohexyl) ethyl] trimethoxysilan (ETMS) were moved under strong stirring with ambient temperature with 24.44 gs (0.1 Mol) Diphenyldimethoxysilan (DPDMS), 5.44 gs (0.015 Mol) to (3-glycidoxypropyl) tetramethyldisiloxan (BGTS), 6.54 gs (0.03 Mol) Pyromellitsäuredianhydrid and up to 3.00 gs (0.05 Mol) SiO<sub>2</sub> (10.00 gs Organosol TM (Kieselöl into 2-Propanol, SiO<sub>2</sub> salary in the Sol = 29.9%, fa to Bavarian)).

Under strong touching and ice cooling were min given to the resulted white suspension drop by drop 18 gs 0.1 n HCl within 5. After finished addition became 14 h with ambient temperature weitergerührt. With increasing response time a clear Sol formed from the at first available

suspension. The product was dried with 40 C DEG and a final pressure from 10-20 mbar 0.5 h abrotiert, 5 h in the Umlufttrockenschrank under vacuum (7 mbar, 45 DEG C) and submitted to a meal process (Red Devil, fa Erichsen). On this occasion, one receives a rieselfähiges powder with a viscosity minimum from 80 to 95 Pa.s at a glaze temperature in the area of from 95 to 105 C DEG, a middle density of 1.26 gs / cm <3> and a grain dimensions distribution from 10-100 mu m. The powder shows thermosetting behaviour after the glaze process what was proved by DSC investigations. The coating powder is electrostatic with a conventional hand spray gun (fa Wagner-ESB) on aluminium tins (Al 99.5 mill finish, pretreated with alkaline Tensid (Almeco TM fa handle)) applicable. The coated aluminium tins were treated 20 min to 120 min with from 120 to 150 C DEG in the Umlufttrockenschrank thermally. The resultant closed, clear cover from 10-25 mu m of thickness shows very good liability (Gt 0/1, TT 0/1).

#### Example 10

24,63 gs (0.1 Mol) [beta - (3,4-Epoxyhexyl) ethyl] trimethoxysilan (ETMS) were moved under strong stirring with ambient temperature with 24.44 gs (0.1 Mol) Diphenyldimethoxysilan (DPDMS), 2.3 gs (0.01 Mol) Dodecandicarbonsäure (DD) and up to 6 gs (0.1 Mol) SiO<sub>2</sub> (20.00 gs Organosol (Kieselsol into 2-Propanol, SiO<sub>2</sub> salary in the Sol = 29.9%, fa to Bavarian)) (mixture A). In parallel a mixture B was produced as follows: To 18 gs 0.1 n HCl 11.61 gs (0.1 Mol) Maleinsäure were added in helpings. After finished addition became with ambient temperature 10 min weitergerührt, until a clear mixture had originated.

Under strong touching and ice cooling mixture B was min given to mixture A drop by drop within 30. After finished addition became 4 h with ambient temperature weitergerührt. With increasing response time a clear Sol formed from the at first available suspension. The product was dried with 40 C DEG and a final pressure from 10-20 mbar 0.5 h abrotiert, 5 h in the Umlufttrockenschrank under vacuum (7 mbar, 45 DEG C) and submitted to a meal process (Red Devil, fa Erichsen). On this occasion, one receives a rieselfähiges powder with a viscosity minimum from 6.5 to 10 Pa.s at a glaze temperature in the area of from 90 to 100 C DEG, a middle density of 1.29 gs / cm <3> and a grain dimensions distribution from 10-100 mu m. The powder shows thermosetting behaviour after the glaze process what was proved by DSC investigations. The coating powder is electrostatic with a conventional hand spray gun (fa. Wagner-ESB) on aluminium tins (Al 99.5 mill finish, pretreated with alkaline Tensid (Almeco TM , fa handle)) applicable. The coated aluminium tins were treated 20 min to 120 min with from 120 to 150 C DEG in the Umlufttrockenschrank thermally. The resultant closed, clear cover from 10-25 mu m of thickness shows very good liability (Gt 0/1, TT 0/1).

#### Example 11

24,63 gs (0.1 Mol) [beta - (3,4-Epoxyhexyl) ethyl] trimethoxysilan (ETMS) were moved under strong stirring with ambient temperature with 24.44 gs (0.1 Mol) Diphenyldimethoxysilan (DPDMS) and up to 3.00 gs (0.05 Mol) SiO<sub>2</sub> (10.00 gs Organosol TM (Kieselsol into 2-Propanol, SiO<sub>2</sub> salary in the Sol = 29.9%, fa to Bavarian)) (mixture A). In parallel a mixture B was produced as follows: To 18 gs 0.1 n HCl 11.61 gs (0.1 Mol) Maleinsäure were added in helpings. After finished addition became with ambient temperature 10 min weitergerührt, until a clear mixture had originated.

Under strong touching and ice cooling mixture B was min given to mixture A drop by drop within 30. After finished addition became 4 h with ambient temperature weitergerührt. With increasing response time a clear Sol formed from the at first available suspension. The product was dried with 40 C DEG and a final pressure from 10-20 mbar 0.5 h abrotiert, 5 h in the Umlufttrockenschrank under vacuum (7 mbar, 45 DEG C) and submitted to a meal process (Red

Devil, fa Erichsen). On this occasion, one receives a rieselfähiges powder with a viscosity minimum from 8.4 Pa.s at a glaze temperature in the area of from 85 to 95 C DEG, a middle density of 1.29 gs / cm <3> and a grain dimensions distribution from 10-100 mu m. The powder shows thermosetting behaviour after the glaze process what was proved by DSC investigations. The coating powder is electrostatic with a conventional hand spray gun (fa. Wagner-ESB) on aluminium tins (Al 99.5 mill finish, pretreated with alkaline Tensid (Almeco TM , fa handle)) applicable. The coated aluminium tins were treated 20 min to 120 min with 120 C DEG to 150 C DEG in the Umlufttrockenschrank thermally. Closed, clear covers resulted from 10-25 mu m of thickness.

#### Example 12

24,63 gs (0.1 Mol) [beta - (3,4-Epoxyhexyl) ethyl] trimethoxysilan (ETMS) were moved under strong stirring with ambient temperature with 24.44 gs (0.1 Mol) Diphenyldimethoxysilan (DPDMS) (mixture A). In parallel a mixture B was produced as follows: To 18 gs 0.1 n HCl were given under strong touching 0.36 gs (0,006 Mol) gamma-AlO (OH) in helpings. For the originating clear solution were added afterwards under strong touching 11.61 gs (0.1 Mol) Maleinsäure in helpings. After finished addition became with ambient temperature 10 min weitergerührt, until a clear mixture had originated.

Under strong touching and ice cooling mixture B was min given to mixture A drop by drop within 30. After finished addition became 4 h with Raumtemperatur weitergerührt. With increasing response time a white, steady mass formed from the at first available suspension. The product was dried with 40 C DEG and a final pressure from 10-20 mbar 0.5 h abrotiert, 5 h in the Umlufttrockenschrank under vacuum (7 mbar, 45 DEG C) and submitted to a meal process (Red Devil, fa Erichsen). On this occasion, one received a rieselfähiges powder with a middle density from 1.29 gs / cm <3> and a grain dimensions distribution from 20-100 mu m. The powder shows thermosetting behaviour after the glaze process what was proved by DSC investigations. The coating powder is electrostatic with a conventional hand spray gun (fa Wagner-ESB) on aluminium tins (Al 99.5 mill finish, pretreated with alkaline Tensid (Almeco TM fa. Handle)) applicable. The coated aluminium tins were treated 20 min with 130 C DEG in the Umlufttrockenschrank thermally. The resultant closed, clear cover from 10-20 mu m of thickness shows good liability to the substrate (Gt 0/1, TT 0/1).

#### Example 13

24,63 gs (0.1 Mol) [beta - (3,4-Epoxyhexyl) ethyl] trimethoxysilan (ETMS) were moved under strong stirring with ambient temperature with 24.44 gs (0.1 Mol) Diphenyldimethoxysilan (DPDMS) and 6.54 gs (0.03 Mol) Pyromellitsäuredianhydrid.

Under strong touching and ice cooling were min given to the resulted white suspension drop by drop 18 gs 0.1 n HCl within 5. After finished addition became 14 h with ambient temperature weitergerührt. With increasing response time a clear Sol formed from the at first available suspension. The product was dried with 40 C DEG and a final pressure from 10-20 mbar 0.5 h abrotiert, 5 h in the Umlufttrockenschrank under vacuum (7 mbar, 45 DEG C) and submitted to a meal process (Red Devil, fa Erichsen). On this occasion, one receives a rieselfähiges powder with a middle density from 1.26 gs / cm <3> and a grain dimensions distribution from 10-100 mu m. The powder shows thermosetting behaviour after the glaze process what was proved by DSC investigations. The coating powder is electrostatic with a conventional hand spray gun (fa. Wagner-ESB) on aluminium tins (Al 99.5 mildly finish, pretreated with alkaline Tensid (Almeco TM , fa handle)) applicable. The coated aluminium tins were treated 20 min to 120 min with from 120 to 150 C DEG in the Umlufttrockenschrank thermally. The resultant closed, clear cover from

10-25  $\mu\text{m}$  of thickness shows very good liability (Gt 0/1, TT 0/1).

#### Example 14

24,63 gs (0.1 Mol) [beta - (3,4-Epoxyhexyl) ethyl] trimethoxysilan (ETMS) were moved under strong stirring with ambient temperature with 12,22 gs (0.05 Mol) Diphenyldimethoxysilan (DPDMS) (mixture A). In parallel a mixture B was produced as follows: To 10,8 gs 0.1 n HCl 5,8 gs (0.05 Mol) Maleinsäure were added in helpings. After finished addition became with ambient temperature 10 min weitergerührt, until a clear mixture had originated.

Under strong touching and ice cooling mixture B was min given to mixture A drop by drop within 30. After finished addition became 4 h with ambient temperature weitergerührt. With increasing response time a clear reaction mixture formed from the at first available murky suspension. The product was dried with 40 C DEG and a final pressure from 10-20 mbar 0.5 h abrotiert, 5 h in the Umlufttrockenschrank under vacuum (7 mbar, 45 DEG C) and submitted to a meal process (Red Devil, fa Erichsen). On this occasion, one receives a rieselfähiges powder with a middle density from 1.29 gs / cm <3> and a grain dimensions distribution from 20-100  $\mu\text{m}$ . The powder shows thermosetting behaviour after the glaze process what was proved by DSC investigations. The coating powder is electrostatic with a conventional hand spray gun (fa. Wagner-ESB) on aluminium tins (Al 99.5 mill finish, pretreated with alkaline Tensid (Almeco TM , fa handle)) applicable. The coated aluminium tins were treated 20 min with 130 C DEG in the Umlufttrockenschrank thermally. The resultant closed, clear cover from 10-20  $\mu\text{m}$  of thickness shows good liability (Gt 0/1, TT 0/1).

#### Example 15

A mixture of 25,3 ml Glycidoxypropyltrimethoxysilan, 80,3 ml Phenyltrimethoxysilan, 16,8 ml Kieselsol 300-30 (30 %-ig, fa Bavarian), 10 ml water and 0,52 ml hydrochloric acid was intensely stirred, until the temperature of the mixture rose by the reaction warmth on from approx. 45 to 50 C DEG. Then the mixture was evaporated immediately in the rotation evaporator at a bath temperature by approx. 50 C DEG. When no more solvent went over, a viscous liquid material which could be pulverised while cooling off had originated. While warming up the powder on 200 C DEG hot hot plate the powder melted under effervescence thin-liquidy on and slowly hardened within from 10 to 15 minutes. There originated a clear, highly shining layer.

#### Example 16

27,6 ml Phenyltrimethoxysilan, 17 gs Diphenylsilanol, 14 gs Tetramethylammoniumhydroxid x 5 H<sub>2</sub>O and 10 gs H<sub>2</sub>O were intensely stirred, until the mixture warmed itself up by the reaction warmth on from approx. 45 to 50 C DEG. After the dry in the rotation evaporator one received a powder which hardened very thin-liquidy aufschmolz and with 200 C DEG within from 1 to 2 hours (decomposition of the Tetramethylammoniumhydroxids).

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Claims of DE19817785

1. Parties, aufschmelzbare and thermally härbare mass, show extensively the condensates K which are derived from at least to one hydrolysierbaren Silan and if necessary to one or several hydrolysierbaren metal connections and to itself in central atoms M of the condensates K find groups A which allow a wide condensation of the condensates at least 70% of the central atoms M one or several in it engaged, not hydrolysierbare organic groups R by which a part can be substituted by with the central atoms M of co-ordinated complicated-pedagogic species, and go through the condensates K in the temperature area of from 50 to 200 C DEG a viscosity minimum in the area of 10 mPa.s to 150 Pa.s.
2. Mass after claim 1, thereby marked that it concerns with at least 75 and mainly at least 85% of the central atoms M silicon atoms.
3. Mass after any of the claims 1 and 2, thereby marked that the condensates show K at least 5 and until 300, mainly at least 10 and up to 200 central atoms M.
4. Mass after any of the claims from 1 to 3, thereby marked that the central atoms different by silicon M are selected from the group Al, Ti and Zr.
5. Mass after any of the claims from 1 to 4, thereby marked that at least 80 and mainly at least 90% of the central atoms order M of at least one organic group R.
6. Mass after any of the claims from 1 to 5, thereby marked, that the numerical ratio x all together in the condensates K to available central atoms M to the sum in these central atoms to located ones, a wide condensation to allowing groups A 1: From 2 to 20: 1, mainly 1: From 1 to 10: 1, amounts.
7. Mass after any of the claims from 1 to 6, thereby marked that one wide condensation of the condensates K to allowing groups A are selected from Hydroxy-, Alkoxy-, Aryloxy-, Acyloxy-, Enoxy-and Oximgruppen.
8. Mass after any of the claims from 1 to 7, thereby marked, that the organic groups R are selected at least partly from sterically hindered groups, in particular if necessary substituted C6-10-Arylgruppen and (cyclo) aliphatischen groups with a steric obstruction which is at least immediately of those one Isopropylgruppe.
9. Mass after any of the claims from 1 to 8, thereby marked that the organic groups R are selected at least partly from groups which can enter a thermal and/or photo-chemical polypolyaddition or condensation reaction catalyzed if necessary.
10. Mass after claim 9, thereby marked that the organic rests R polymerisierbare carbon carbon-multiple connections and/or Epoxid rings enclose.
11. Mass after any of the claims 9 and 10, thereby marked that a part of the groups R of Epoxid rings and another part of the groups R of amino groups shows and/or that a part of the groups R Carbon shows carbon-multiple connections and another part of the groups R Thiolgruppen.
12. Mass after any of the claims from 1 to 11, thereby marked that a part of the groups R of fluorine atoms shows.
13. Mass after any of the claims from 1 to 12, thereby marked that it contains, in addition, a thermally activateable or releaseable polypolymerisations or addition catalyst for the organic interlinking and/or one or several substances which release a catalyst for the wide condensation of the available condensates at raised temperatures.
14. Mass after any of the claims from 1 to 13, thereby marked that the condensates put out K at

least 50 Gew.-%, mainly at least 80 Gew.-%, the measures.

15. Mass after any of the claims from 1 to 14, thereby marked that it contains, in addition, fillers and/or nanopartikuläre oxide powders in an amount from up to 25 Vol.-%.
16. Procedures for coating of substrates with a powder varnish, thereby marked that the powder varnish encloses the mass after any of the claims from 1 to 15.
17. Procedures after claim 16, thereby marked that the powder varnish is raised by electrostatic powder varnish.
18. Procedures after any of the claims 16 and 17, thereby marked that it concerns with the substrates those from metals, plastics, glass or ceramics.
19. use of the mass after any of the claims from 1 to 15 in a powder varnish for the production of wear-steady and anti-corrosive coatings on metals.
20. Procedures to the production of a steady, aufschmelzbaren thermally härtbaren mass, extensively the controlled hydrolytische polycondensation of one or several hydrolysierbaren connections of the silicon and/or suitable Silanole, if necessary in combination with one or several hydrolysierbaren metal connections and at least one part of the used connections disposes of not hydrolysierbare organic groups R and/or from suitable precondensates to reach to condensates which go through a viscosity minimum in the area of 10 mPa.s to 150 Pa.s in the temperature area of from 50 to 200 C DEG, used and the next distance from in the polycondensation or during these educated brief components.
21. Procedures after claim 20, thereby marked that it concerns with at least one of the used hydrolysierbaren connections a Silan with one or two Phenylgruppen as groups R.
22. Procedures after any of the claims 20 and 21, thereby marked that at least one of the used hydrolysierbaren connections is a Silan with Epoxygruppen-and/or Methacrylgruppen and/or Vinyl groups-containing rest R.
23. Procedures after any of the claims from 20 to 22, thereby marked that at least one part of the used hydrolysierbaren metal connections is in komplexierter form.
24. Procedures after any of the claims from 20 to 23, thereby marked that the metal connections are selected from such of Al, Ti and Zr.
25. Procedures after any of the claims from 20 to 25, thereby marked that a thermally activateable or releaseable catalyst is annexed to the mass for the wide condensation of the condensates K and/or the polyaddition or polycondensation more accordingly of organic groups R as well as if necessary a photo-chemically activateable catalyst for the polyaddition / polycondensation more accordingly of organic groups R.